Thermodynamics of the Sequestration of Carbon Dioxide in Methane Hydrates in Porous Media

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Concerns about potential effects of rising carbon dioxide levels in the atmosphere have stimulated interest in a number of carbon dioxide sequestration studies. One suggestion is the sequestration of carbon dioxide as clathrate hydrates by injection of carbon dioxide into methane hydrates. Energy-supply research estimates indicate that natural gas hydrates in arctic and sub-seafloor formations contain more energy than all other fossil fuel deposits combined. The simultaneous sequestration of carbon dioxide into deposits of natural gas hydrates, if possible, represents a potentially efficient and cost effective option for the sequestration of carbon dioxide.

Data in the literature show that the conversion of bulk methane hydrate into carbon dioxide hydrate is thermodynamically favored. These results are not directly applicable to naturally occurring hydrates, because the hydrates in these locations are embedded in sediments. In addition, naturally occurring hydrates are normally made up of mixtures of natural gases, often predominately methane. The thermodynamics of any potential conversion of hydrates involving methane to carbon dioxide hydrate would therefore be affected by the size of the pores in which the conversion would take place, as well as the composition of the gas. We have developed a model that can be used to interpret or predict hydrate formation in porous media for any pore size distribution, allowing for the calculation of the heats of formation of these hydrates in porous media as a function of pore size and temperature. These results are applied to mixtures of methane and carbon dioxide. This allows for a preliminary assessment of the thermodynamic feasibility of converting hydrates formed from methane to carbon dioxide hydrate in porous media involving various size pores.

Introduction

The build up of carbon dioxide in the atmosphere has become of great interest due to the potential of this gas to play an important role in greenhouse effects, and its reported potential to induce global warming on the order of $2 – 5$ K over the next century[1]. As a result of these concerns, researchers have suggested various methods to sequester carbon dioxide in order to remove it from the atmosphere. One sequestration scheme[2] is the injection of carbon dioxide into methane hydrate deposits, which it is suggested could result in the simultaneous sequestration of the carbon dioxide and the liberation of methane (which could then be collected and used as a clean fuel). Gas hydrates are crystalline structures that involve a lattice made up of hydrogen-bonded water molecules. This lattice includes cavities that can be occupied by gas molecules. Gas hydrates (such as methane hydrate) form under low temperature – high pressure conditions, both above and below the freezing point of water. Due to the large size of naturally occurring methane hydrate deposits, this represents a vast potential supply of methane. The simultaneous sequestration of carbon dioxide and liberation of methane represents a potentially cost-effective sequestration scheme for carbon dioxide. Since much of the worlds naturally occurring methane hydrates are in sediments below the ocean floors or in permafrost regions, it is necessary to consider the effects of porous media on the formation of gas hydrates.

Studies by Makogon[3] in sandstones suggested that the pressure required for hydrate formation increased as the pore size was decreased. Differences in chemical potentials and interfacial forces between the bulk and pore water affect hydrate formation in pores. Handa and Stupin[4] studied methane and propane hydrates in silica gel of 7.5 nm nominal pore radius, and Uchida et al.[5] investigated the properties of methane hydrate in three porous Vycor glass samples with pore radii of 25 nm, 15 nm, and 5 nm. In a recent work[6] the authors presented measurements for propane hydrate formation in silica gels of nominal pore radii of 7.5 nm, 5.0 nm, 3.0 nm, and 2.0 nm. Injection of carbon dioxide into methane hydrate deposits with the subsequent sequestration of the carbon dioxide and liberation of the methane would result in hydrates in equilibrium with a mixture of free carbon dioxide and methane. No results for hydrates in porous media formed from gas mixtures have been reported in the literature. In this work we consider the prediction of the equilibrium pressure for mixtures of methane and carbon dioxide in porous media based on a statistical thermodynamic model. The model is then used to estimate enthalpies of dissociation of hydrates formed from mixtures of carbon dioxide and methane in porous media.

Model Description

Munck et al.[7] presented a single equation involving T_f and P_f (the temperature and pressure under which the hydrate forms) that can be used to predict hydrate formation conditions under bulk conditions. This equation can be written as

$$\frac{\Delta \boldsymbol{m}_W^0}{RT_0} - \int_{T_0}^{T_f} \frac{\Delta H_w}{RT^2} dT + \int_0^{P_f} \frac{\Delta V_w}{R\overline{T}} dP - \ln\left(\boldsymbol{g}_w X_w\right) + \sum_i \boldsymbol{h}_i \ln\left(1 - \sum_k Y_{ki}\right) = 0$$

(1)

In eq (1), $\overline{T} = (T_0 + T)/2$, T_0 is the temperature of the standard reference state (T = 273.15 K, P = 0), $\Delta \boldsymbol{m}_W^0$ is the chemical potential difference between the empty hydrate lattice and pure water in the reference state, $\boldsymbol{h}_i$ is the ratio of the number of cavities of type i to the number of water molecules in the hydrate lattice, and Y_i denotes the probability of a cavity of type i being occupied by the guest molecule. The probability Y_i is given in terms of the fugacity of the hydrate guest in the gaseous state (f_i) and the Langmuir adsorption constant (C_i) by $Y_{ki} = C_{ki} f_k / (1 + \sum_j C_{ji} f_j)$. Additionally, $\Delta H_W = \Delta H_W^0 + \Delta C_p^0(T')(T - T_0)$, where ΔH_W^0 is a reference enthalpy difference between the empty hydrate lattice and the pure water phase at the reference temperature, ΔC_p^0 is the reference heat capacity difference, and ΔV_W is the volume difference between the empty hydrate and pure water (at T_0), and is assumed constant. Also note that the values used for ΔC_p^0, ΔH_W^0, and ΔV_W depend on whether the equilibrium involves liquid or solid water. In this work, the temperature dependence of the Langmuir constants will be accounted for by using the form presented by Munck et al.[7] This form is given by $C_{ki} = (A_{ki}/T)\exp(B_{ki}/T)$, where A_i and B_i are experimentally fit parameters, and are dependent on which guest molecule is present, as well as which of the hydrate structures is formed. To consider hydrate formation in porous media, eq. (1) must be modified to include the effect of the relevant interface on the activity of the water. After

making the necessary modifications in the region where the equilibria involve liquid water, eq. (1) becomes[8]

$$\frac{\Delta \boldsymbol{m}_W^0}{RT_0} - \int_{T_0}^{T_f} \frac{\Delta H_w}{RT^2} dT + \int_0^{P_f} \frac{\Delta V_w}{R\overline{T}} dP - \ln(\boldsymbol{g}_w X_w) + \sum_i \boldsymbol{h}_i \ln(1 - \sum_k Y_{ki})$$
$$+ V_L \frac{2\cos(\boldsymbol{q})\boldsymbol{s}_{hw}}{RT_f r} = 0 \qquad (2)$$

In eq. (2), V_L is the molar volume of water in the pure water state, $\grave{e}$ is the contact angle between the aqueous phase and the hydrate, $\boldsymbol{s}_{hw}$ is the surface tension between the aqueous and hydrate phases (taken as 0.0267 J/m^2 as given by Clennell et al[9]), and r is the radius of the pores in the porous medium. Eq. (2) can be used for all temperatures above the ice point of water in the corresponding pore of radius r. Below the ice point one recovers eq. (1) since the current model assumes there are no surface effects between ice and hydrate.

Results and Discussion

Figure 1a shows the results of using eq. (1) to predict the hydrate equilibrium pressure for bulk mixtures of methane and carbon dioxide. Also shown in the Figure are the experimental data given in Sloan.[10] We note that all of the experimental data are in the liquid water region, and involve Structure I hydrates. We also note that for temperatures slightly above those depicted in Fig 1a as part of the calculated surface, the mixture involves liquid carbon dioxide, and the predictions become less accurate.

Surfaces similar to Fig. 1a can be constructed using eq. (2) for hydrate formation in porous media. For example, Figure 1b shows the results for pore radii of 3, 6, and 9 nm. The upper right hand corner of Fig. 1b shows a dramatic change in slope in the logarithm of the equilibrium pressure, due to the effects of the magnitude of the pressure on the state of the carbon dioxide involved in the equilibria. Also note the non-linearity of the surface in Fig. 1b for larger temperatures (and therefore pressures), which indicates the changing character of the carbon dioxide involved in the equilibria.

The equilibrium pressure of mixtures in porous media is a function of 3 variables (temperature, mole fraction, and pore radius). As a result, one can examine cross-sections of the 3 dimensional surface (which lies in a 4 dimensional space) other than the one shown in Fig. 1b. For example, in Figure 2 the logarithm of the equilibrium pressure is shown as a function of 1/T and 1/r for five values (0.0, 0.25, 0.5, 0.75, and 1.0) of the mole fraction of carbon dioxide in the mixtures. Due to the higher hydrate equilibrium pressure in porous media, changes in the state of the carbon dioxide in the mixture take place at lower temperatures than they do in the bulk. This can lead to different types of equilibria taking place at the same temperature in different size pores in the porous media. Fig. 2a shows the surfaces for pressures where both components (CO_2 and CH_4) remain in gaseous form. We note that as the mole fraction of CO_2 increases, the equilibrium pressure decreases due to the lower equilibrium pressure for hydrates formed from pure gaseous CO_2, as compared to that of those formed from pure gaseous CH_4. Higher temperatures and/or smaller pore sizes result in higher equilibrium pressures. At some of these higher pressures CO_2 liquefies. Due to the larger equilibrium pressure for hydrates formed from liquid CO_2 as compared to those for hydrates formed from either gaseous CH_4 or gaseous carbon dioxide, equilibria involving liquid CO2 have significantly higher equilibrium pressures. Under conditions where either the temperature is high enough or the pore size is small enough,

mixtures with larger mole fractions of CO_2 have higher equilibrium pressures than pure methane hydrates (as seen in Fig. 2b), suggesting the presence of liquid carbon dioxide. In addition to the limitations of calculations involving liquefied components, the form of the Langmuir constants employed here may not be as accurate as more complicated forms. This potential source of inaccuracy will be investigated in future work.

As is made clear from these preliminary results, the evaluation of the potential sequestration of carbon dioxide by injection into sediment deposits containing methane hydrates may require accurate methods of predicting hydrate equilibrium pressures when the mixtures involve liquid carbon dioxide and gaseous methane. Since the determination of liquid phase densities and fugacities can
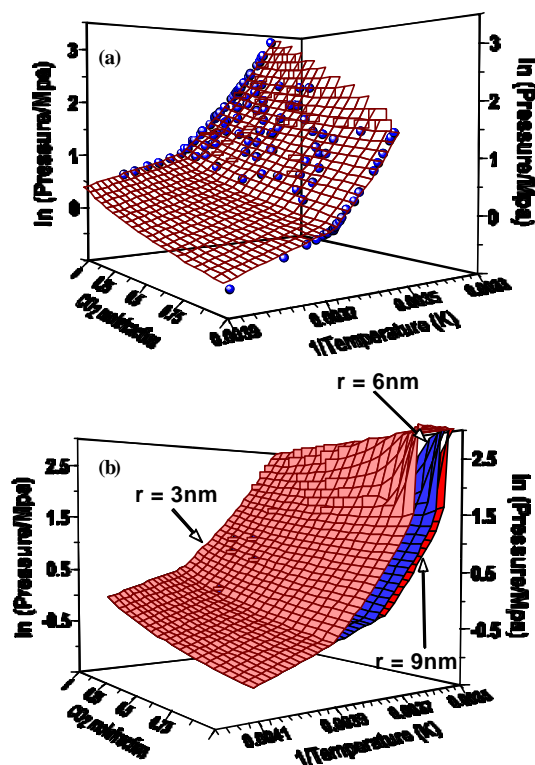

Figure 1. **(a)** Surface showing predicted equilibrium pressures for CO_2/CH_4 mixtures and experimental data for bulk hydrate formation. **(b)** Calculated surfaces for equilibrium pressures for CO_2/CH_4 mixtures in porous media with pore radii of 3, 6, or 9 nm.

involve larger errors than those for the gaseous phase,[10] great care must be taken in developing such predictions.

In addition to calculating the equilibrium pressure, eq. (2) can be used along with the Clausius-Clapeyron equation $d(\ln(P))/d(1/T) = -\Delta H / zR$ to estimate the enthalpy of formation of mixtures of carbon dioxide and methane in porous media. In the above equation, z is the gas compressibility, and is calculated using
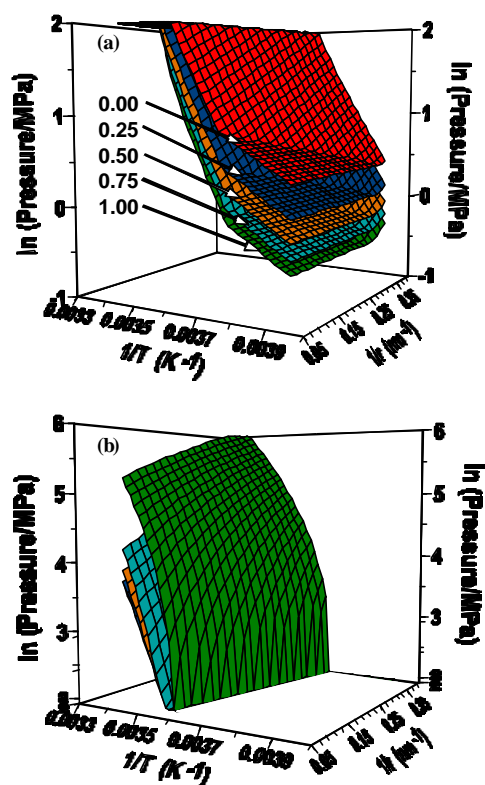
Figure 2. Calculated surfaces for equilibrium pressures for CO_2/CH_4 mixtures having CO_2 mole fractions of 0.0, 0.25, 0.5, 0.75, and 1.0 in porous media.

Figure 3. **(a)** Calculated surface showing the enthalpy of dissociation for CO_2/CH_4 mixtures in a porous medium having pore radii of 5.0 nm. **(b)** The enthalpy of dissociation at 273.2 K as a function of the mole fraction of carbon dioxide for the bulk (dotted trace) as well as in porous media with 3 and 5 nm pores.

the Soave-Redlich-Kwong equation of state. Figure 3a shows the results of calculation of the enthalpy of dissociation for mixtures of

carbon dioxide and methane in a porous medium containing pores with 5 nm radii. Results from Figure 3a for a temperature of 273.2 K are shown in Fig. 3b, along with the results for pores having a 3 nm radius and for bulk calculations (dotted trace). We note that the very rapid changes evident in Figs 2 and 3 for pure CO_2 (a mole fraction of 1.0) are due to its liquefaction (due to the larger equilibrium pressures necessary in porous media). The calculations presented here for hydrate formation involving liquefied states may have more limitations than do those only involving gases, and as such these preliminary results will only be examined from a qualitative standpoint at this time. The difference between the enthalpy of dissociation in porous media and that in the bulk for a mixture with a mole fraction of 0.2 or greater seems to increase as the pore size decreases. For mole fractions below this there seems to be a more complicated behavior. This suggests that CO_2 sequestration in porous media via conversion of methane hydrate into CO_2 hydrate may be even more favored, thermodynamically, than it is in the bulk. While intriguing, quantitative interpretation of these results will require further investigation.
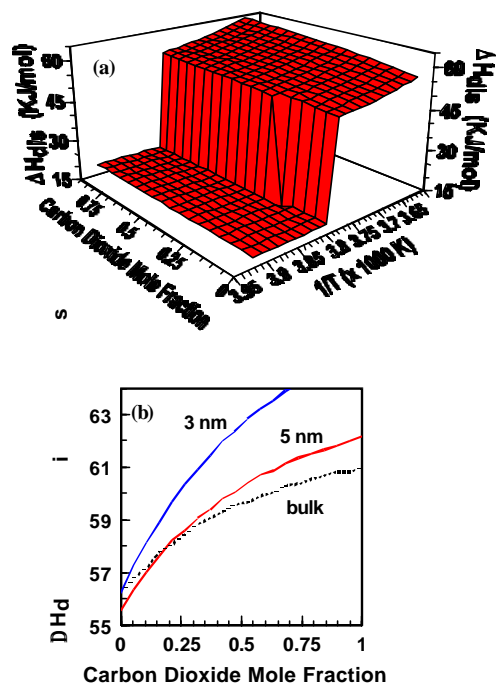
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